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URBAN AEROSOL MODELING

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Accurate numerical schemes have been developed for simulation of the condensation/evaporation processes with vapor conservation for a single component aerosol. These have been incorporated in modules which allow simulation of aerosol dynamics in models for dispersion and transport.

The coagulation process can be simulated by these methods with high accuracy. In coagulation simulation errors can be reduced to any desired level by choices of width and size interval. It has been shown that the method of fractional steps give excellent results with large savings in computer time.

The condensation/evaporation process with vapor conservation has been simulated numerically through the use of a new Eulerian-Lagrangian numerical technique. With this technique numerical dispersion and diffusion can be reduced to any desired level.

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ABSTRACT

Accurate numerical schemes have been developed for simulation of the coagulation and condensation/evaporation processes with vapor conservation for single component aerosol. These schemes have been incorporated in modules which permit simulation of aerosol dynamics in models for atmospheric dispersion and transport. Published comparisons have established the accuracy of these modules and procedures for their inclusion in atmospheric models.

The coagulation process can be simulated by the methods developed with high accuracy. Comparisons with analytical solutions, where available, and mass conservàtion have provided tests of accuracy. In simulation of coagulation by developed methods, errors can be reduced to any desired level automatically by choice of widths and size interval. For incorporation of the coagulation rate process in any atmospheric dispersion and transport model, it has been shown that the method of fractional steps gives excellent results with very large savings in computer time for large-scale simulations.

The condensation/evaporation process with vapor conservation has been simulated numerically through use of a new Eulerian-Lagrangian numerical technique developed during this project. With this technique, numerical dispersion and diffusion can be reduced to any desired level. The method of fractional steps has been shown to be valid for incorporating the condensation/evaporation process in atmospheric dispersion

and transport models.

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LIST OF SYMBOLS

A	velocity slip constant
B	velocity slip constant
b	coagulation rate coefficient
c	monomer mass concentration
c_v	monomer equilibrium vapor mass concentration
D	particle diffusion coefficient
e	continuum condensation/evaporation rate coefficient
G_z	gravitational sedimentation velocity
g	aerosol density function in logarithmic transform coordinate
H	mixing height
J	logarithmic transform of particle mass
K	eddy diffusivity
Kn	Knudsen number
m	particle mass
m_1	monomer molecular mass
n	aerosol number density function
q	logarithmic mass transformation scaling factor
R	particle radius
s	monomer saturation ratio
T	temperature
t	time
U	x-component of mean wind velocity
V_d	deposition velocity
$\bar{v}$	mean thermal speed of particles

x	distance in direction of mean wind
y	distance transverse to mean wind
z	vertical distance above ground level
β	transition correction to coagulation coefficient
δ	Dirac delta function
κ	Boltzmann's constant
$\dot{\nu}_N$	homnogeneous nucleation rate
Ψ	particle growth rate by condensation/evaporation

SECTION 1

INTRODUCTION

The urban aerosol is associated with various adverse effects, such as reduced visibility, inadvertent weather modification, and increased incidence of respiratory disease. An understanding of this association requires, among other factors, knowledge of the ambient aerosol size and composition distributions. In spite of this, there currently are no validated models for the urban aerosol which deal with the complexity of the dynamical processes producing these distributions. These dynamical processes include nucleation, coagulation, condensation/evaporation, and deposition in addition to atmospheric dispersion and transport. Models including these processes are necessary for rational development of aerosol air quality regulations and control strategies. For example, light scattering and absorption are complex functions of the aerosol particle size distribution. Also, the deposition pattern of an aerosol depends on the particle size distribution. Many of the chemical species making up the urban aerosol are produced through the interaction of complex chemical processes and aerosol particles, the details of which vary with particle size and composition. Therefore, the effects of pollutant emissions reduction and control are likely to be nonlinear in character and will depend on a detailed understanding of the dynamical processes responsible for the aerosol particle and composition distributions.

This project has been concerned with development of urban aerosol models which include the dynamical processes shaping the urban aerosol size and composition distributions. The first part of this work has involved validation of data bases and a K-theory model for the super- and sub-micrometer aerosol mass concentration. More recently, work has been proceeded on the development of computer modules for accurate description of the coagulation and condensation/evaporation processes for single component aerosols. These modules can be employed in the K-theory model or other models as desired. Results from work on these modules are summarized here.

SECTION 2

CONCLUSIONS

Accurate and efficient numerical schemes have been developed under this study for simulation of coagulation and condensation/evaporation with vapor conservation. Methods for incorporating these numerical schemes in atmospheric dispersion and transport models have also been investigated. In addition, existing numerical methods for advection and dispersion have been investigated.

For coagulation, we report the following conclusions regarding the simulation of this process and its incorporation in atmospheric dispersion and transport models. The coagulation process is simulated using cubic spline for numerical quadrature and interpolation. Modified Gear's method is used for time integration.

In the context of atmospheric models incorporating coagulation we have noted the following. Fromm's method has been shown to be an accurate scheme for advection. It compares favorably with the pseudo-spectral method but it requires less computational effort. In simulations, it was estimated that advection and diffusion only took about 2% of the total CPU time; therefore it is worthwhile to use a higher order explicit scheme for advection. The objective is to achieve the same accuracy while reducing the number of grid points used, thereby reducing the number of calculations for aerosol dynamics processes.

In this study, orthogonal collocation on finite elements is shown to be better than finite difference for diffusion. It

can approximate the boundary condition accurately because it uses more grid points to evaluate the derivatives than does finite difference. The numerical results we have obtained for coagulation provide proof of the capability of the method of fractional steps to simulate accurately aerosol coagulation and transport.

A robust numerical scheme for condensation/evaporation should be free of numerical dispersion while numerical diffusion is minimized. Eulerian numerical schemes create numerical dispersion, whereas Lagrangian schemes do not.

In our work, we have modified and combined Varoglu and Finn's method with Neumann's method because of the requirements of the condensation/evaporation term. This new method has been successful. This method is more accurate than the linear finite element method over the whole computational domain. For continuum evaporation, $\psi = -em^{1/3}$, the method gives also good agreement with the analytical solution.

In this study, this new method has been applied to investigations of the classical problem of "Ostwald ripening." The accuracy of the method has been demonstrated in the special case of continuum evolution wherein the asymptotic case is excellent in the long time limit. More generally, we have shown that aerosol evolution involves development of asymptotic limit distribution in analogy with the asymptotic limit distributions observed for the coagulation process.

The simulation of the condensation/evaporation process involves simultaneous solution for the rate of change of the

conserved vapor. In addition, these processes must be incorporated in atmospheric dispersion and transport models. For a large scale urban simulation, the simultaneous solution by an implicit numerical scheme with a matrix technique for 10^4 - 10^5 unknowns is no trivial task. In this work the method of fractional steps has been used in the simulation. Advection, diffusion, and evaporation are included as follows:

1. Solve the advection and diffusion equation J_{max} times where J_{max} is the number of size classes.
2. Solve the evaporation equation by LFEM at each grid point.
3. Solve the advection and diffusion equation for s.
4. Calculate the source term for vapor due to condensation/evaporation, and update the saturation ratio at that grid point.

If the saturation ratio of the vapor does not change with position - that is, is constant - procedures 3 and 4 are not necessary. The method of fractional steps just outlined decouples the particle and vapor equations. The explicit nature of procedure 4 does not pose a problem, because the source term is counterbalanced by the dilution effect of advection and diffusion. The numerical procedures discussed above for advection and diffusion are employed in urban simulations.

In the context of plume models, it has been demonstrated that the numerical techniques for the condensation/evaporation process yield very accurate results for the very special cases where analytical solutions are available.

SECTION 3

RECOMMENDATIONS

The numerical schemes and approach developed in this work provide one of the first comprehensive studies of aerosol growth in the context of a model for atmospheric dispersion and transport. The modules for coagulation and condensation/evaporation that we have developed have been proven to yield highly accurate simulations of aerosol growth processes in the context of an atmospheric model.

These growth modules should be used in comparisons with approximate methods which have been proposed by others for handling aerosol dynamics. It is also felt that currently available approximate methods are not adequate for atmospheric simulations on the urban scale. It is recommended that new approximate methods be developed using the methods outlined here.

The numerical schemes developed here for coagulation and condensation/evaporation need to be extended to multi-component aerosol dynamics. This will be essential in the study of chemical speciation. Similarly, based on accurate simulation methods, approximate methods will need to be developed.

It is particularly important that field and laboratory aerosol data be obtained with sufficient resolution and accuracy to permit validation of atmospheric aerosol dynamics models. These data should include not only time and space resolved size distributions but also chemical speciation.

SECTION 4

PROCEDURE

GENERAL DESCRIPTION

The aerosol growth processes must be incorporated in a general atmospheric dispersion and transport model. In order to understand how the growth modules enter in such a model, it is useful to illustrate these growth processes in the context of the K-theory model used in work under this project. For a single component aerosol, one studies the evolution of the particle number density function $n(m,x,z,t)$, where $n(m,x,z,t)dm$ is the number of particles having masses in the range m,dm at downwind position x,y at height z at time t. The evolution equation is

$$\frac{\partial n(m,x,y,z,t)}{\partial t} + U(z)\ \frac{\partial n(m,x,y,z,t)}{\partial x} + \frac{\partial}{\partial m}\left[\Psi(m,s)n(m,x,y,z,t)\right] = \frac{\partial}{\partial z}K(z)\ \frac{\partial n(m,x,y,z,t)}{\partial z} + \frac{\partial}{\partial y}K(y)\ \frac{\partial n(m,x,y,z,t)}{\partial y} + G_z(m)\ \frac{\partial n(m,x,y,z,t)}{\partial z} + \tfrac{1}{2}\int_0^m b(m-m',m')n(m-m')n(m')dm' - n(m)\int_0^\infty b(m,m')n(m')dm' + \dot{\nu}_N \qquad (1)$$

This equation is coupled to the following conservation equation for the vapor, given in terms of the saturation ratio, s:

$$\frac{\partial s(x,y,z,t)}{\partial t} + U(z)\ \frac{\partial s(x,y,z,t)}{\partial x}$$

$$= \frac{\partial}{\partial z}\ K(z)\ \frac{\partial s(x,y,z,t)}{\partial z} + \frac{\partial}{\partial y}\ K(y)\ \frac{\partial s(x,y,z,t)}{\partial y}$$

$$- \frac{1}{c_v} \int_0^\infty \Psi(m,s)\, n(m,x,,z,t)\, dm - \frac{1}{c_v}\ m^*\ \dot{\nu}_N \qquad (2)$$

Equations (1) and (2) are subject to the following initial and boundary conditions:

$$n(m,x,y,z,0) = n_o(m,x,y,z),$$

$$s(x,y,z,0) = 0,$$

$$s(0,y,h,t) = 1.0,$$

$$\frac{\partial n(m,x,y,H,t)}{\partial z} = \frac{\partial s(x,H,t)}{\partial z} = 0,$$

$$nV_d(m) = -K\partial n/\partial z - G_z n,\ z = 0$$

$$sV_d(s) = K\partial s/\partial z$$

$$\frac{\partial^2 n}{\partial y^2} = \frac{\partial^2 n}{\partial x^2} = 0,\ x = 0,\ x_{max}$$

$$\frac{\partial^2 n}{\partial y^2} = \frac{\partial^2 n}{\partial x^2} = 0,\ y = 0,\ y_{max}$$

In these equations, $U(z)$ is the x component of the mean fluid velocity, and $K(z)$ is the vertical and $K(y)$ the transverse eddy diffusivity; $G_z(m)$ is the gravitational settling speed for a particle of mass m. $V_d(m)$ is the deposition velocity of a particle with mass and $V_d(s)$ that for the vapor. H is the mixing height. A constant flux condition is assumed for transport into the study area. $\dot{\nu}_N$ is the homogeneous nucleation rate with c_v the vapor mass concentration and m^* the critical nucleus mass. s is the supersaturation.

$\Psi(m,s)$ is the condensation/evaporation growth law for a

particle. $b(m,m')$ is the coagulation coefficient. These quantities are established from the literature for growth and Brownian coagulation in the non-continuous regimes. For $b(m,m')$, the interpolation formula of Fuchs[1] is used to describe Brownian coagulation:

$$b(m,m') = 4\pi(R + R')\ (D + D')\ \beta$$

$$\beta = 1/(1 + 4\ (D + D')/(m^{1/3} + m'^{1/3})(\bar{V}^2 + \bar{V}'^2)^{1/2})$$

$$m = (4/3)\pi R^3 \rho;\ V = (8\kappa T/\pi m)^{1/2}$$

$$D = (kT/6\pi\mu R)\ (1 + Kn(A + Be^{-CKn})^{-1})$$

Coagulation mechanisms other than Brownian have been found to be unimportant for the urban aerosol.[2]

The condensation/evaporation growth law has the form:

$$\Psi(m) = \pi R^2\ V_1\ c_v\ (s - e^{Ke})\pi^{1/2}\ Kn \cdot \left[\frac{1 + Kn\ \frac{4\pi Kn}{3} + 1.016}{\frac{4Kn}{3} + 1}\right]^{-1}$$

where:

$$\bar{V}_1 = \left(\frac{8\kappa T}{\pi m_1}\right)^{1/2};\quad Kn = L/R;\quad L = 2D_{1h}\ (m_1/2\kappa T)^{1/2};$$

$$S = c/c_v$$

m_1 refers to the molecular mass of the condensing/evaporating species. This expression is found to correlate available experimental data satisfactorily over the range $0 < Kn < \infty$.[3]

Numerical techniques for the separate rate processes of coagulation and condensation/evaporation will be examined in detail here.

Numerical Simulation of Pure Coagulation

A variety of methods have been proposed for numerical simulation of coagulation and condensation. Work before 1970 on coagulation has been reviewed by Drake.[4] Since this time, a large number of numerical studies have been carried out in spatially uniform systems.[5,6,7,8] In view of the many numerical approximation schemes which have been proposed, it would be desirable to develop test problems for evaluating these schemes. For very large scale atmospheric aerosol dynamics simulations, approximate methods may be suitable, given the existing uncertainties in input data. The emphasis in this discussion will be on methods of high accuracy which we have employed in simulation studies.

The pure coagulation process is described by the equation:

$$\frac{\partial n(m,t)}{\partial t} = (1/2) \int_{m_*}^{m} dm\, b(m-m',m')\, n(m-m',t)\, n(m',t) - n(m,t) \int_{m_*}^{\infty} dm'\, b(m',m)\, n(m',t) \qquad (3)$$

Simulation of aerosol growth involves particle radii covering around four orders of magnitude $\sim 10^{-8} - 10^{-4}$ cm. The logarithmic transformation suggested by Berry[9] has been employed by us in a number of studies:

$$m(J) = m(J_o) \exp(q(J-J_o)) \qquad (4)$$

J is a positive number greater than or equal to J_o. $m(J_o)$ is the mass of a particle starting at J_o. q is a numerical parameter which can be selected to give equally spaced integer J values. From the definition of the density function,

$$n(m(J)) = g(J)/qm(J) \tag{5}$$

With (3) and (5), eq. (3) becomes:

$$\frac{\partial g(J,t)}{\partial t} = \int_{J_o}^{J_u} dJ'\, b_1(\tilde{J}, J')g(\tilde{J},t)g(J',t)$$

$$- g(J,t) \int_{J_o}^{\infty} dJ' b(J,J')g(J',t)$$

$$- \frac{\partial}{\partial J}\left[\Psi(J)g(J)/qm(J)\right] \tag{6}$$

and

$$J_u = J - \ln 2/q,\ J \geq 2;$$

$$\tilde{J} = J + (1/q)\ \ln[1-\exp(q(J'-J))];$$

$$b_1(\tilde{J},J') = (m(J)/m(\tilde{J}))\ b(m-m',m').$$

with $b(m-m',m')$ given above. The adjustable parameter q has a great advantage in "fine tuning" for mass or diameter spacings to increase numerical accuracy.

The coagulation process can be numerically simulated with high accuracy. We chose methods that optimize both accuracy and efficiency. Accuracy has been studied by comparison with analytical solutions for restricted forms of $b(m,m')$ and with Brownian coagulation by testing for conservation of mass. We use cubic spline for numerical quadrature and interpolation of the coagulation terms. Modified Gear's method is used for time integration. Comparisons noted above show that simulation by these methods is accurate and reliable and that errors can be reduced to any desired level.

Numerical Simulation of Pure Condensation/Evaporation

The pure condensation/evaporation problem with vapor conservation for a single component aerosol is described by the evolution equation:

$$\frac{\partial n(m,t)}{\partial t} + \frac{\partial}{\partial m}\left[\Psi(m,t)\ n(m,t)\right] = 0 \qquad (7)$$

$$\frac{\partial s}{\partial t} = -(1/c_v) \int_{m^*}^{\infty} dm \Psi(m,t) n(m,t) - (1/c_v)\ m^*\ \Psi(m^*,t)\ n(m^*,t) \qquad (8)$$

where m^* is the mass of the smallest stable particle, which in eq. (2) was set equal to zero as an approximation. Ψ and the other terms are discussed above. Eqs. (7) and (8) assume implicitly that the vapor concentration is much less than the concentration of the host gas. This ensures that the condensation/evaporation process is isothermal. Without this condition eqs. (7) and (8) would be coupled to the energy conservation equation, as indeed is the case for rapid growth of aerosols. In the atmosphere, growth processes are sufficiently slow that coupling with the energy equation is not necessary.

If the supersaturation s is controlled externally, eq. (7) is decoupled from eq. (8). In this case the solution of eq. (7) is very simple and can be effected by the method of characteristics.

When S is not externally controlled, eqs. (7) and (8) are coupled, and no analytical solution has been found. Equations (7) and (8) constitute a nonlinear integro-differential equation for n(m,t) and only numerical solution appears to be

feasible. In any event, stable numerical techniques for eqs. (7) and (8) are desirable when these equations are to be combined with coagulation and other processes in general studies of aerosol evolution.

When the supersaturation is held fixed, eq. (7) with a source term and approximate forms for Ψ has been studied both analytically[10,11] and numerically.[8] Equations (7) and (8) with a source term for nucleation have previously been studied numerically[5] through the introduction of various approximations. If source terms are added to eqs. (1) and (3), e^{Ke} is linearized, and the van't Hoff factor for dissolved solute nuclei is included in Ψ, one obtains the familiar evolution equations for the water cloud droplet spectrum.[12] Attempts at a direct numerical solution of the cloud droplet equations have usually shown evidence of numerical instability.[13] Other modelling efforts[14] simply assume a size distribution with time-dependent parameters. It should be pointed out that the cloud droplet size spectrum equations are from a numerical standpoint simpler than eqs. (7) and (8) because the former contain a fixed lower-limit size spectrum due to the presence of dissolved involatile nuclei.

Equation (7) is deceptively simple in appearance. It is worth noting that there is a difference of around ten orders of magnitude in particle mass m between particle diameters of 10^{-7} and 10^{-3} cm if we choose to use m as the independent variable. In the J-space formulation[6] described above for coagulation, Ψ varies by ten orders of magnitude. The Kelvin effect causes

this coefficient to change sign at a certain particle size for a given supersaturation. This coefficient is negative for evaporation and positive for condensation. These factors make the numerical solution of (7) difficult.

Difficulties in the numerical solution of first-order hyperbolic equations, such as eq. (7) are well known. This is evidenced by the numerous published attempts at numerical solutions of similar hyperbolic equations (in the simulation of advection, for example). The problem is that most numerical schemes for hyperbolic equations give rise to numerical dispersion and numerical diffusion. The numerical dispersion, caused by the combination of large phase errors and insufficient damping of short waves, manifests itself by the unphysical wakes behind and ahead of the simulated regions of high concentration. Numerical diffusion lowers the peak values of the concentration distribution but increases the values around the peak. Numerical methods with "upwinding" can remove numerical dispersion but create unrealistic numerical diffusion.[13] Numerical methods without upwinding, such as the finite-element method with linear basis functions[14,15,16] do not introduce much numerical diffusion but create numerical dispersion. Such dispersion is undesirable for simulation of condensation/evaporation because dispersion increases with time and, for prolonged simulations, finally dominates and creates numerical instability. Also, numerical dispersion may erase the real "signatures" of the condensation/evaporation processes.

Many methods have been tried to reduce dispersion, such as the introduction of a dissipative term in the Galerkin finite-element formulation[17,18] or the use of filtering schemes.[19] These have not been found to be suitable for condensation/evaporation simulation.

A robust numerical scheme for condensation/evaporation should be free of numerical dispersion while minimizing numerical diffusion. Eulerian numerical schemes create numerical dispersion, whereas Lagrangian schemes do not suffer from this difficulty. Using the approach of Bonnerot and Jamet,[20] Varoglu and Finn[21] derived a finite-element method incorporating characteristics of the diffusion-convection equation. This scheme is free of numerical dispersion. Similar to Finn's moving finite-element method is the Lynch and O'Neill[22] approach to the Stefan problem, and the advection-diffusion problem. Recently, Neuman[23] derived an Eulerian-Lagrangian numerical scheme for the diffusion-convection equation that is also free from numerical dispersion and controls numerical diffusion.

In our work we have modified and combined the methods of Varoglu and Finn and of Neuman with the Lynch and O'Neill method for the numerical solution of coupled equations (7) and (8).

Condensation and evaporation with constant supersaturation were simulated numerically and compared with the exact solution of eq. (7) for a number of cases. A method such as the finite-element method, LFEM,[15] gives severe dispersion at the left of the peak of a distribution. This dispersion increases in magnitude with time until it dominates the solution, which then becomes unstable. The present method is a modification of that of Varoglu and Finn. It does not require the introduction of a new grid point at the in-flow boundary for each time level as is the case for the finite element method. Thus, it requires less computational effort. Any Eulerian numerical method - such as finite difference, Fromm's method[24] and the cubic spline scheme for the first derivative with Gear's method for time integration - suffers from numerical dispersion. The present method does not. Moreover, the present method conserves the total number concentration to any desired level of accuracy.

Our method has also been applied to continuum evaporation where $\Psi \sim -m^{1/3}$. Because for the continuum model the smaller the particle, the higher is the evaporation rate, the use of Finn's method alone results in the loss of a large number of grid points as particles disappear at the outflow boundary. One of the remedies we have found is to use Neuman's concept[23] of advection and diffusion. The procedure is as follows. One uses the modified Finn's method to obtain a new aerosol distribution at a time $t + \Delta t$. Then, one uses the cubic spline scheme for interpolation onto the fixed grids. The resulting number distribution is the initial condition for the next time step.

Neuman[23] used linear interpolation for advection and diffusion. However, linear interpolation gives too much numerical diffusion in this case. The use of cubic spline interpolation is very satisfactory, although one must be careful to anticipate the possibility that a small noise or oscillation may exist near the inflow boundary. Comparisons with analytical solutions gave excellent agreement with the analytical solution. It is also worth noting that, for pure evaporation, LFEM with natural inflow boundary conditions gives very accurate results with negligible dispersion at the right of the peak of a unimodal function. If a fixed inflow boundary condition is used, LFEM gives severe dispersion and an unstable result. On the other hand, even if natural inflow and outflow boundary conditions are used for the pure condensation growth problem, $\Psi \sim +m^{1/3}$, LFEM gives unacceptable dispersion and unstable results. Our numerical experiments have shown that the evaporation problem is quite different from the condensation problem from the numerical point of view, even though both problems are governed by the same equation (7). It can also be concluded that the choice of boundary conditions is extremely important if meaningful solutions are to be obtained. The latter conclusion is also well known in solving the advection-diffusion equation.[25] Finally, it should be pointed out that numerical methods with upwind differencing, such as the donor cell method,[13] when applied to eq. (7) give unacceptable numerical diffusion, although they do not suffer from numerical dispersion. In our studies, the donor cell method gives large and unacceptable

deviations from the analytical solutions for both total number concentration and the peak value. Thus numerical schemes employing upwind differencing, such as the sectional method[11] may not be suitable for these aerosol growth calculations.

Consider now simulation of eqs. (7) and (8) with constant vapor concentration. The Kelvin effect is included. In this case, the condensation/evaporation interface does not change with time and has a fixed location. For this case of constant vapor concentration, the problem can be solved either with n or with $\theta = \forall n$ as the independent variable. If θ is used as the dependent variable, it has the advantage that it is equal to zero at the condensation/evaporation interface. Natural boundary conditions are used. In these studies, LFEM is used for the evaporation region, and the modified Finn method is used for the condensation region. The number density at the interface is found by cubic spline interpolation. There is no numerical dispersion.

Where vapor is not constant and is conserved according to eqs. (7) and (8), the interface moves to larger particle diameters with decrease in supersaturation. Equations (7) and (8) form a coupled nonlinear integrodifferential equation with moving boundary. In this case the evaporation region expands as the vapor depletes. If LFEM with natural boundary conditions is used to solve the problem for the whole domain, severe oscillation near the interface and instability result. Thus, a finite-element method with moving grids is necessary for the sake of accuracy and numerical stability. Recently,

Lynch and O'Neill[25] used a finite-element method with moving grids to solve a Stefan problem. The deformation of the grids is similar to that derived by Murray and Landis.[26] Therefore in the evaporation regime we reformulate eq. (7) and define the moving grid's velocity in the spirit of Murray and Landis. The numerical procedure consists of three parts. First, Finn's method is used to solve eq. (7) for the entire condensation/evaporation regime. Continuous application of Finn's method alone results in the loss of a large number of grid points, as mentioned before. Second, we use cubic spline interpolation to obtain the number distribution near the interface. This interpolation is necessary to ensure accuracy and stability. Finally, LFEM on the moving grid system in the evaporation regime is used to complete the domain of solution. Equation (8) is solved explicitly. For the parameter employed in our numerical studies,[27] most of the change in the total mass concentration of particles occurs in only a short initial period. Therefore, the use of small time steps and an explicit solution of eq. (8) are satisfactory. Variable time steps can be used when the integral in eq. (8) becomes very small.

Our method[27] has been applied to investigations of eqs. (7) and (8) corresponding to the classical problem of "Ostwald ripening."[28] The accuracy of the method has been demonstrated in the special case of continuum evolution where the asymptotic solution of Lifshitz and Slezov[29] applies. Agreement with this asymptotic case is excellent in the long time limit. More generally, we have shown that aerosol evolution by (7) and (8)

involves development of asymptotic limit distributions in analogy with the asymptotic limit distributions observed for the coagulation process.

The combined coagulation and condensation process with vapor conservation has also been studied using the methods described above. Various tests including special case analytical solutions, support the accuracy of our methods.

Coagulation and Condensation/Evaporation in an Atmospheric Plume

Equation (1) was intended to illustrate the general structure of an atmospheric dispersion and transport model including aerosol growth processes. The applicability of a first-order closure model to aerosol growth requires that the characteristic coagulation and condensation/evaporation times be much greater than the Lagrangian time scale of turbulence. This condition is met approximately in the downwind fields of sources; close to sources, turbulence may be determined principally by the characteristics of the sources, and a sub-grid scale analysis would be necessary.

We have studied,[2,30,31] separately, the coagulation and condensation/evaporation processes in the context of the atmospheric dispersion and transport model given in eq. (1). For these studies, we have chosen the crosswind line source as the best source configuration for numerical technique development. There are a number of advantages in the choice of the infinite crosswind line source plume. The need for a subgrid

scale numerical treatment is eliminated. Analytical solutions exist for simple forms of U(z) and K(z), which permit accurate tests of numerical methods. Also, a number of numerical schemes for advection and dispersion have already been tested for the crosswind line source. Finally, the considerable uncertainty surrounding the crosswind eddy diffusivity does not enter.

For this model, eq. (1) for only coagulation and an infinite crosswind line source becomes:

$$\frac{\partial n(m,x,z,t)}{\partial t} + U(z)\ \frac{\partial n(m,x,z,t)}{\partial x} = \frac{\partial}{\partial z} K(z)$$

$$\cdot\ \frac{\partial n(m,x,z,t)}{\partial z} + \frac{1}{2}\int_0^m b(m,m_1)\,n(m-m_1,x,z,t)\,n(m_1,x,z,t)\,dm_1$$

$$- n(m,x,z,t)\int_0^\infty b(m,m_1)\,n(m_1,x,z,t)\,dm_1 + G_z(m)$$

$$\cdot\ \frac{\partial n(m,x,z,t)}{\partial z} \qquad (9)$$

where coordinate x is in the direction of the mean wind, and z is the vertical distance above ground level. U(z) is the mean x component of atmospheric velocity and K(z) is the vertical eddy diffusivity. Equation (9) is to be solved with initial and boundary condition:

$$n(m,x,z,o) = 0,$$

$$n(m,o,h,t) = \frac{Q_o}{U(h)}\,\delta(z-h)\,f(m),$$

$$\frac{\partial n}{\partial z} = 0, z = H;\quad nV_d(m) = -K\frac{\partial n}{\partial z} - G_z(m)\,\frac{\partial n}{\partial z} \qquad (10)$$

where Q_o is the source strength, h its height above ground level, f(m) is the source number density function, H is the

atmospheric mixing height, and V_d is the particle deposition velocity.

Not much work has been done on simulation of coagulation in spatially inhomogeneous system. Petit[32] simulated the coagulation of particle size distributions in plumes using a Gaussian dispersion approach. Shieh[33] combined a Gaussian plume model and a finite difference model to simulate the advection, diffusion, deposition and coagulation of an urban aerosol. The trapezoidal rule was used in the integration of the coagulation terms. However, no effort was made to check the accuracy and the reliability of the numerical schemes. Eltgroth and Hobbs[34] simulated the evolution of particles in the plumes of coal-fired power plants. The model includes the effects of advection, diffusion, coagulation, gravitational settling, gas-to-particle conversion and interaction with the ambient air. Log-normal distributions were used for each mode of a model trimodal distribution and it was assumed that the evolution preserved the log-normal distributions. Three moment equations were solved for each mode. In order to use the moment equations, the form of wind speed, gravitational settling velocity, diffusivities, gas-to-particle conversion rate and coagulation coefficients were also restricted. The initial number concentrations, however, were sufficiently low that coagulation was rapidly suppressed by dispersion of the plume.

Our studies differ from all of these in that we directly solve eqs. (9) and (10) with no approximations other than numerical differencing.

The coagulation term is simulated by methods described above. Obviously, a fully implicit scheme for eq. (9) would be prohibitive for a large scale simulation. We, therefore, use the method of fractional steps.[35] A fully implicit scheme for solving a three dimensional aerosol model requires simultaneous solution of $IM \cdot JM \cdot KM \cdot J_{max}$ equations. For IM = 20 in X direction, JM = 20 in Y direction, KM = 10 in Z direction and J_{max} = 30 size classes, a simultaneous solution for the 120,000 unknowns would not be feasible; the method of fractional steps used in our calculation removes the necessity of carrying out simultaneous solutions for these unknowns. In our studies, we have shown that the method of fractional steps is a reliable scheme for treating multidimensional nonlinear problems, which include aerosol coagulation.

Our study of various numerical methods in solution of eq. (9) has shown the following.

Fromm's method has been shown to be an accurate scheme for advection. It compares favorably with the pseudo-spectral method but it requires less computational effort. It was estimated that advection and diffusion only took about 2% of the total CPU time in our simulations; therefore it is worthwhile to use a higher order explicit scheme for advection.[36] The objective is to achieve the same accuracy while reducing the number of grid points used, thereby reducing the number of calculations for aerosol dynamics processes.

In our studies, orthogonal collocation on finite elements has been found to be better than finite difference for diffusion.

It can approximate the boundary condition accurately because it uses more grid points to evaluate the derivatives than does finite difference.

Cubic spline interpolation and quadrature provide an accurate numerical scheme for coagulation. The numerical results given in the last section are useful for comparisons with other numerical methods. Again, the method of fractional steps is an efficient technique for incorporating multiple rate processes in multidimensional nonlinear problems, including coagulation and condensation/evaporation, as discussed below.

The corresponding equation to eq. (9) for condensation/evaporation is as follows:

$$\frac{\partial n(m,x,y,z,t)}{\partial t} + U(z) \frac{\partial n(m,x,y,z,t)}{\partial x} + \frac{\partial}{\partial m}[\Psi(m,s)n(m,x,y,z,t)] = \frac{\partial}{\partial z} K(z) \frac{\partial n(m,x,y,z,t)}{\partial z} + G_z(x) \frac{\partial n(m,x,z,t)}{\partial y} \qquad (11)$$

This equation is coupled to the conservation equation for the vapor which we give in terms of the saturation ratio, s:

$$\frac{\partial s(x,z,t)}{\partial t} + U(z) \frac{\partial s(x,z,t)}{\partial x} = \frac{\partial}{\partial z} K(z) \frac{\partial s(x,z,t)}{\partial z} - \frac{1}{c_v} \int_0^\infty \Psi(m,s)n(m,x,z,t)dm \qquad (12)$$

Equations (11) and (12) are subject to the initial and boundary conditions analogous to those for the coagulating plume.

The numerical solution of the coupled integro-partial differential eqs. (11) and (12) presents a challenging problem. The simultaneous solution by an implicit numerical scheme using

a matrix technique for 10^4 - 10^5 unknowns is no trivial task. In our work the method of fractional steps has been used in the simulation. Advection, diffusion, and condensation/evaporation are included as follows:

1. Solve the advection and diffusion equation J_{max} times, where J_{max} is the number of size classes.
2. Solve the evaporation equation by LFEM at each grid point.
3. Solve the advection and diffusion equation for s.
4. Calculate the integral term in eq. (2) which is a source term for vapor due to evaporation, and update the saturation ratio at that grid point.

If the saturation ratio of the vapor does not change with position - that is, is constant - procedures 3 and 4 are not necessary. The method of fractional steps just outlined decouples eqs. (11) and (12). The explicit nature of procedure 4 does not pose a problem, because the source terms is counter-balanced by the dilution effect of advection and diffusion.

We have found that dispersion of a plume of condensing/evaporating aerosol with vapor conservation can be simulated numerically by the methods outlined here. For the special case where an analytical solution is possible, we have shown that the numerical solution converges to the analytical solution with a reduction in step size; consequently the error in numerical simulation can be reduced to any desired level. In these comparisons, the validity of the method of fractional steps has been proven with the attendant advantage over fully implicit schemes.

With the methods described in part here, many interesting problems in aerosol dynamics can now be studied. Our accurate numerical procedures also provide the basis for development and testing of approximate aerosol growth equations.

SECTION 5

RESULTS AND DISCUSSION

Modules for simulation of the coagulation and condensation/evaporation processes are necessary in atmospheric aerosol models. For example, it appears to be well established that in many urban areas, a major part of the mass of suspended particulate matter is formed by products of atmospheric chemical reactions. Also, fine particles from primary sources attach at important rates by coagulation onto ambient particles.[6] While simplified modules for these processes may be desirable, it is first necessary to establish results from application of coagulation and condensation/evaporation modules with verifiable accuracy. This phase of development has now been completed.

Accurate and efficient modules have been produced under this study for simulation of coagulation and condensation/evaporation with vapor conservation. Methods for incorporating these modules in atmospheric dispersion and transport models have been established.

With the "J-space" transformation, the coagulation process has been simulated accurately and efficiently by using cubic spline for numerical quadrature and interpolation and modified Gear's method for time integration. Coagulation in plumes has been simulated accurately and efficiently using the method of fractional steps, which has been established through this work as a reliable scheme for treating multidimensional nonlinear problems of the type arising in atmospheric aerosol dynamics.

A new, accurate, numerical scheme has been developed for simulation for condensation/evaporation processes. This new method has been carefully checked in a number of special cases where analytical solutions are available. Where analytical solutions are not available, it has been shown that numerical dispersion and diffusion can be reduced to any desired level. It has been demonstrated that dispersion of a plume of condensing/evaporating aerosol can be simulated numerically by the methods outlined here. For the special case where an analytical solution is possible, it has been shown that the numerical solution converges to the analytical solution with a reduction in step size; consequently the error in numerical simulation can be reduced to any desired level. In these comparisons, the validity of the method of fractional steps has been proven with the attendant advantage over fully implicit schemes. From these and other studies it has been demonstrated that the finite-element method using linear basis functions and natural boundary conditions yields accurate numerical solutions for the condensation/evaporation process.

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